

## **Project 95159**

### **Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste**

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#### **RESULTS TO DATE: Electrochemical Emission Spectroscopy**

In this work, the examination of electrochemical noise data comprised three main approaches: one, a computer simulation of the anodic and cathodic activity relating to corrosion on a metal surface; two, experimental modeling of the electrochemical environment inside nuclear waste storage containers and collection of EN generated; and three, Wavelet analysis of the EN data from the first two parts. The simulation of EN proved to be effective in replicating the EN data of both general and pitting corrosion. Using competition mechanisms for the anodic and cathodic sites on the surface, the long-term, low-frequency data generated by localized pitting corrosion was reproduced. Disabling one or more of the rules of the simulation eliminated the low-frequency character of the data, and eliminating all of the rules effectively reproduced general corrosion noise. The simulation accuracy benefited from comparison to experimental data, and conversely, it improved the EN analysis by providing theory for the underlying mechanisms. The experimental electrochemical cell modeled the important factors in nuclear waste storage containers for this EN study; mainly increased temperature and the concentrations of corrosion-inducing or inhibiting chemicals. It also provided a platform for studying how the EN was affected by the competing chemicals. The third and most important aspect of this study was Wavelet analysis. It proved to be an effective means of studying EN data generated by corrosion processes. Taking a deterministic approach, WA collects information about the underlying corrosion processes that has not been reliably obtained by previously established analysis methods. The primary advantage WA has over competing methods like FFT and MEM is that it is specifically adapted to the characteristics of EN. WA is able to work with the rapid, overlapping fluctuations in current data and with the changing mean. It also analyzes the data at a number of frequency resolutions and retains data in the temporal domain. Both FFT and WA are frequency domain analysis methods. WA identifies the EN generated by different corrosion processes in the frequency domain, but FFT is simply not able to provide the detail and resolution that wavelets can. Wavelet analysis' division of information into a smooth data crystal and many detail data crystals allow it to more-accurately depict the high-frequency and/or low-amplitude noise fluctuations key to EN. These are the fluctuations that contain information on the underlying corrosion processes, but, in FFT, that information is mostly lost when analyzed at only one frequency resolution and depicted on a log scale. In WA, the increasing resolution of subsequent crystals provides information on a number of time scales, which is key to analyzing the different types of corrosion because of the natural frequencies of the corrosion mechanisms. In this work, it was shown that WA identifies when general corrosion is the prevailing corrosion type because it has an inherently high frequency. Pitting corrosion is similarly identified by its lower frequency. WA also identifies when there is a mix of corrosion types by examining the contributions from both low- and high-frequency crystals to the total signal energy. Depictions of the wavelet coefficients in the time domain identify at what time a corrosion type becomes dominant or fades based on when the standard deviation of the wavelet coefficients increases or drops, respectively. It also accurately determines the average duration for many corrosion events, and it is able to resolve the repassivation times of single events. WA also determined that nitrate ions are effective in inhibiting both general and localized corrosion, while nitrate ions are less effective at inhibiting localized corrosion and instead promote general corrosion. Phosphate ions promote general corrosion, and chloride ions induce pitting (in accordance with literature).

## Crack Propagation Studies

1. For AISI 4340 steel in NaOH solution at 70 degree celcius, the results show that the susceptibility to caustic SCC increases with NaOH concentration. No crack propagation is observed in 1 M and 5 M NaOH solutions. Individual brittle micro fracture events are observed at low crack growth rate in 6 M NaOH solution. In more concentrated NaOH solution (8 M and 12 M), on the other hand, the noise in the (electron) coupling current displays periodic features that are best observed by Fourier transformation. It is postulated that caustic cracking in this high strength steel in the more concentrated caustic environments advances by many micro cracks occurring simultaneously. A transient in the coupling current signals each micro crack advance and, since many events occur at any given time, the coupling current appears as semi random fluctuations on a high mean.
2. Hydrogen embrittlement has been postulated to be the mechanism for environment-assisted cracking in high strength steels in caustic environments.
3. Calculations yield a micro fracture dimension of 49 microns. Acoustic emission test results confirm the assumption that the individual transients indeed represent individual crack events in most of the cases.
4. Crack growth rate decreased and KISCC increased drastically in the case of L-T orientation specimens compared to S-L orientation specimens. This decrease in crack growth rate and increase in KISCC in the case of L-T orientation specimens is due to the L-T orientation specimens possessing higher fracture toughness in comparison to the S-L specimens
5. The kinetics of repassivation also changed significantly with the specimen orientation. These results show the anisotropic nature of Stress Corrosion Cracking in AISI 4340 steel under caustic conditions.
6. The SCC crack front is concave in shape (Crack grows predominantly along the sides). This is because of the electrochemical nature of the stress corrosion cracks. The sides, which have a high proximity to the external cathodes, grow extensively in comparison to the centre of the specimen, which is relatively far off from the external cathodes. The CGR along the sides was found to about 7-20 times the CGR along the centre of the specimen. These results clearly prove that it is the external cathodes and not the crack flanks that sustain bulk of the cathodic reaction.
7. In some specimens there was extensive crevice formation due to Teflon coating delamination, above and below the side grooves of the compact tension specimens. This crevice formation has a profound effect on the crack propagation. The crack growth rate (CGR) of the samples that had the problem of crevice corrosion was negligible in comparison to the samples that didn't have the problem (CGR of a sample with no crevice was about 0.5 cm/day and that of a specimen with crevice was about 0.1 mm/day at 70 degree celcius in 8 M NaOH solution). The reason for this drastic decrease in crack growth rate in the case of samples with crevice corrosion can be explained as follows.

**Lenhart, English and Macdonald, while investigating the phenomenon of nucleation and growth of pits in buffered chloride solution by using in situ optical microscopy, made the following two observations:**

1. Each pit that nucleated on the surface and grew had associated with it a hemisphere of influence (HOI) which is produced by a high concentration of hydrolyzed metal ions. No new, stable pits nucleated under the HOI of an existing pit.
2. The overlaps of HOIs from neighboring pits inevitably lead to the death of one of the pits.

Just like pitting, crevice and stress corrosion phenomena also come under the category of localized corrosion phenomena. Hence, a crevice or a stress corrosion crack could have their own HOIs. Since the size of the crevice is much larger than the size of the stress corrosion crack, and since the crevice and crack are in close proximity to each other, the crack could come under the HOI of the crevice and hence get

cathodically polarized. This would decrease the crack growth rate. The HOIs of the crack and the crevice could also overlap leading to the Darwinian death of the weak stress corrosion crack. These two reasons would collectively lead to the drastic decrease in CGR of the stress corrosion crack.

### **Continued Development of the Theory of Passivity**

Ellipsometry, XPS, and AFM were used to analyze the passive film formed on iron in a borate buffer solution (with a pH of 8.4) at ambient temperature (23 degree celcius), 50 degree celcius, and 75 degree celcius. The results are consistent with those predicted by the Point Defect Model (earlier work on this project). These results will allow for better estimates in the model parameters by revealing the possible structure of the film and the valence state of iron within the film. In addition the ellipsometry results indicate that when EDTA (a chelating agent) is in solution, only a single layer forms (the barrier layer).

The ellipsometry measurements were used mainly to measure the thickness of the passive film as a function of applied potential and temperature in solutions containing EDTA. At ambient temperatures the thickness of the film varied linearly from approximately 8 angstroms (roughly the size of a lattice parameter -Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>) at lower formation potentials in the passive region to about 17 angstroms near the oxygen evolution potential. The maximum thickness measured at ambient temperature was 17 angstroms and the maximum thickness increased to around 20 angstroms at 50 degree celcius, and almost 50 angstroms at 75 degree celcius. These values are just first calculations and should be viewed as estimates for the thickness values. Nevertheless, the calculations do reveal an increase in the oxide thickness with temperature as would be expected. Mott-Schottky analysis reveals that the defect density of the films decrease slightly with both temperature and voltage indicating that as the films grow (in response to changes in temperature or applied voltage), the films become less defective. Ellipsometry was also used to determine the thickness of the film or films that formed in the borate buffer solution when EDTA was not added. Fits, based on a single layer model, could not be obtained. However, if a two-layer regression model was used, thicknesses for the two oxide layers (an inner and outer layer) were obtained. The analysis reveals that an inner layer forms, with a thickness of about 30 angstroms, at the lowest potential in the passive region. The inner layer thickness does not vary much with potential through the passive range. On the other hand, the outer layer thickness changes from a minimum of 0 angstroms to a maximum thickness of approximately 2 angstroms. It should be noted that the optical constants of the inner layer were the same as those used in the single-layer model used to calculate the thicknesses in solutions containing the EDTA. This would suggest that the EDTA only removes the outer precipitated layer, which allows for the inner layer (believed to be responsible for passivity) to be studied without introducing measurement artifacts due to the formation of a precipitated outer layer.

XPS was used to determine the valence state of iron in the film. While the ellipsometry work was performed in-situ, the samples had to be removed for the XPS work. Studies have shown that the films formed on iron in borate buffer solution at potentials greater than +0.2 VSCE are stable in air for many days. Therefore, oxides were grown above this potential for this work. The results show that the film is nearly all Fe<sup>3+</sup>. No Fe<sup>2+</sup> peaks were observed in the data. However, due to the “over-shadowing” of the elemental iron (Fe<sup>0</sup>) and the Fe<sup>3+</sup> peaks in the scan, a detection limit of 10% is estimated for Fe<sup>2+</sup> species in the film. This is consistent with other work that estimates the Fe<sup>2+</sup> present in the film to be less than 5% [1]. With this knowledge, it can be estimated that if the structure of the film formed on iron in borate buffer solutions is Fe<sub>3</sub>O<sub>4</sub>, at least 20 % of the iron sites would have to be vacant and very few interstitial sites would be occupied by an iron cation with a valence state of 2. This information would seem to point to the fact that the film would be a p-type semi-conductor (with iron vacancies being acceptor sites) and this is contradictory to the n-type behavior of the film as measured by Mott-Schottky analysis and photo-current measurements [2]. Consequently, we believe that the Fe<sub>2</sub>O<sub>3</sub> or similar structure (LAMM phase [3]) as a film is closer to a defective structure suggested by others. The defects responsible for n-type behavior would then be iron interstitials and oxygen vacancies in the film and we believe this to be the case. Earlier fits of the PDM to impedance data, where only oxygen vacancies were assumed present, yielded a correct estimation of the thickness, but the predicted current density was several orders of magnitude lower than measured. By the use of the PDM, it is implicitly argued that the iron interstitials must be present to account for the higher current densities. However, the iron film growth according to the PDM is accounted for via the formation

of oxygen vacancies. For this reason, both iron interstitials and oxygen vacancies are suggested to be present in the passive film

Finally, AFM was performed ex-situ on films grown above +0.2 VSCE (for the reasons stated earlier). Originally, this work was done to estimate the average surface roughness for use in the models used in the ellipsometry work (RMS thickness = 30 angstroms). However, further observation of the AFM images revealed that the film contained a nano-crystalline microstructure (grain sizes = 15-20 nm), as has been found by others [4].

To conclude, the knowledge gained from the above work will be used to alter the PDM to better describe the oxide growth on iron. We will be better able to account for the reactions occurring and decrease the number of parameters in the model to allow for more accurate fits. The model will then be applied to describe the oxide film growth as a function of potential, pH, and temperature in borate buffer solutions. From this information, it is the hope of those working on the project that predictions on damage due to general corrosion will be better accounted for.

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**DELIVERABLES:** Publications in Peer Reviewed Journals and Conference Proceedings 1. J. Liu and D. D. Macdonald, "The Passivity of Iron in the Presence of Ethylenediaminetetraacetic Acid II. The Defect and Electronic Structures of the Barrier Layer", *J. Electrochem. Soc.*, 148 (11), B425-B430 (2001) 2. Vankeerberghen, M., and D. D. Macdonald, "Predicting Crack Growth Rate vs. Temperature-Behaviour of Type 304 Stainless Steel in Dilute Sulfuric Acid Solutions", *Corros. Sci.*, 44, 1425-1441 (2002). 3. Macdonald, D. D., et.al., "High temperature on-line monitoring of water chemistry and corrosion control in water cooled power reactors; Report of a coordinated research project 1995-1999", *Proc. IAEA-TECDOC-1303*, International Atomic Energy Agency (IAEA), Vienna, Austria, July 2002. 4. Liu, S. and D. D. Macdonald, "Fracture of AISI 4340 Steel in Concentrated Sodium Hydroxide Solution", *Corrosion*, 58, 835-845 (2002). 5. Sikora, E. and D. D. Macdonald, "Nature of the Passive Film on Nickel", *Electrochimica Acta*, 48, 69-77 (2002). 6. Macdonald, D. D., "Comments on "Electrochemical Transients During the Initial Moments of Anodic Oxidation of Aluminum" by Huiguan Wu and Kurt Hebert, *Electrochimica Acta*, 47, 1373-1383 (2002)", *Electrochimica Acta*, 48, 127-130 (2002) 7. Macdonald, D. D., "Controlling IGSCC in BWR Coolant Circuits", *Proc. 2ndst DAWAC Conf.*, Int. Atomic Energy Agency, Prague, Czech Republic, Nov. 26-29, (2002) 8. Macdonald, D. D. and G. R. Engelhardt, "Deterministic Prediction of Localized Corrosion Damage A Reflective Review of Critical Issues", *J. Corros. Sci. Engin.*, 6, Paper C066 (2003). 9. Macdonald, D. D., "Internal/External Environment Coupling in Stress Corrosion Cracking", *J. Corros. Sci. Engin.*, 6, Paper C065 (2003). 10. Vankeerberghen, M. and D. D. Macdonald, "Calculating the Temperature Maximum and the Lower Potential Limit for the Crack Growth Rate in Type 304 SS Using the CEFM", Paper 03250, *CORROSION2003*, San Diego, CA, March 2003. 11. Macdonald, D. D. and Gomez-Duran, M., "Stress Corrosion Cracking of Sensitized Type 304 Stainless Steel in Thiosulfate Solution: I. Fate of the Coupling Current", *Corrosion Science*, 45, 1455-1471 (2003) 12. Englehardt, G. and D. D. Macdonald, "Estimation of Corrosion Cavity Growth Rate for Predicting System Service Life", *Corrosion Science*, 46(5), 1159-1187 (2004). 13. Englehardt, G. and D. D. Macdonald, "Unification of the Deterministic and Statistical Approaches for Predicting Localized Corrosion Damage: I. Theoretical Foundation", *Corrosion Science*, in press (2003). 14. Macdonald, D. D., "Passive Films: Nature's Exquisitely Nano-Engineered Protection System", *Current Applied Physics*, 4(2-4), 129-132 (2004). 15. Macdonald, D. D. and G. Englehardt, "Theory For The Deterministic Prediction Of Pitting Corrosion Damage On Aluminum", *Proc. Electrochemical Society*, Orlando, FL, Oct. 12-17, 2003. 16. Ahn, S., HyukSang Kwon, and D. D. Macdonald, "The Role of Chloride Ion in Passivity Breakdown on Nickel", *Proc. Electrochemical Society*, Orlando, FL, Oct. 12-17, 2003. 17. Macdonald, D. D. and Gomez-Duran, M., "Stress Corrosion Cracking of Sensitized Type 304 Stainless Steel in Thiosulfate Solution: I. Fate of the Coupling Current", *Corrosion Science*, 45, 1455-1471 (2003) 18. Gomez-Duran, M.

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25. M. T. Smith and D. D. Macdonald, "Wavelet Analysis of Electrochemical Noise Data," Paper #05355, CORROSION 2005, Houston, TX, April 2005.

26. D. D. Macdonald, Predicting the Future from the Past in Corrosion Science and Engineering, Eurocorr 2004, Nice, France, Sept. 12-17, 2004. (Plenary). Paper in conference proceedings (will be published in 2005).

27. D. D. Macdonald and G. Engelhardt, Challenges in Predicting the Accumulation of Localized Corrosion Damage-A Review of Critical Issues, Egyptian Corrosion Soc., 23rd Conf. Corrosion Problems in Industry, Ras Sedr, Egypt, Dec. 6-9, 2004. (Invited)

#### Presentations

1. D. D. Macdonald, "The Holy Grail: Deterministic Prediction of Corrosion Damage Thousands of Years into the Future", International Workshop on the Prediction of Long Term Corrosion Behavior in Nuclear Waste Systems", Chateau de Cadarache, France, Nov. 26-29, 2001.

2. D. D. Macdonald, "A Brief History of Electrochemical Impedance Spectroscopy", Centenary Meeting of the Electrochemical Society, Philadelphia, PA, May 12-17, 2002. Invited.

3. D. D. Macdonald, "Recent Advances in the Theory of Stress Corrosion Cracking", Institute of Nuclear Safety Systems, Osaka, Japan, May 26-30, 2002. Invited.

4. D. D. Macdonald, "Passivity, the Enabler of Our Metals-Based Civilization", University of Florida, July 12, 2002. Invited.

5. D. D. Macdonald, "Passivity and Passivity Breakdown", Georgia Institute of Technology, July 12, 2002. Invited.

6. D. D. Macdonald, "Can We Predict the Future in Corrosion Science", 2002 DOE Corrosion Contractors Meeting, Brookhaven National Laboratory, September 13-14, 2002.

7. D. D. Macdonald, "Can Corrosion Science Predict the Future", presented in receipt of the U. R. Evans Award, British Corrosion Institute, Cardiff, Wales, October 23, 2002. Invited.

8. D. D. Macdonald, "Passive Films, Nature's Exquisitely Nano-Engineered Protection System", AMN-1, The Macdiarmid Institute for Advanced Materials and Nano Technology, Terepapa, Wellington, New Zealand, February 13, 2003. Invited.

9. M. Vankeerberghen and D. D. Macdonald, "Calculating the Temperature-Maximum and the Lower Potential Limit for the Crack Growth Rate in Type 304 SS Using the CEFM", CORROSION 2003, (NACE International, Houston, TX), San Diego, CA March 17-27, 2003.